THE CHLORINATION OF 1-P-NITROPHENYL-3-METHYLBUTADIENE-1,3

A THESIS

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THEORETICAL

Investigations have been carried on in this laboratory for a number of years for the purpose of thoroughly formulating the mode of addition of halogens, specifically bromine and chlorine to conjugated dienes.

According to the electronic theory of polarization, a conjugated diene system should polarize in at least two ways. Under these conditions it is possible for addition reactions to take place on terminal or adjacent carbon atoms of the chain.

Experimentally it has been shown that bromine[1] and chlorine[2] add to butadiene-1,3 in the 1,2 and 1,4 positions, the relative amounts being determined by the nature of the solvent and the temperature at which the reactions are conducted.

The initial attack on the diene system is by positively polarized halogen, and the system strives in every way possible to facilitate the reaction. Only by attack at a terminal carbon atom can an electrophilic reagent call into play the electron supplying ability of the entire conjugated system.[3]

The following graphic examples will illustrate the possible isomers expected when one mole of chlorine is added to butadiene-1,3:

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[1] Farmer, Lawrence and Thorpe, J. Chem. Soc., 729 (1928).

[2] Muskat and Northrup, J. Am. Chem. Soc., 52, 4043 (1930).

[3] E. E. Royals, "Advanced Organic Chemistry," Prentice Hall Incorporated, New York, 1954, p. 398.

The intermediate carbonium ion is a resonance hybrid; the positive charge is effectively distributed between carbon atom 2 and 4 of the conjugated system producing both 1,2 and 1,4 isomers.

(1) 

1,4 addition

(2) 

1,2 addition

It has been determined experimentally that the 1,4 isomer predominates (80%) as a result of the rearrangement of the 1,2 isomers.[4] Generally 1,4 addition is the rule for addition of halogens to butadiene and its purely aliphatic derivatives, such as isoprene[5], 2,3-dimethylbutadiene[6] and 1,4-dimethylbutadiene.[7]

The replacement of one of the terminal hydrogen atoms of butadiene-1,3 by the highly electronegative phenyl group has resulted in a compound which adds bromine[8] and chlorine[9] in the 3,4 positions.

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[4]Farmer, et al., op. cit.

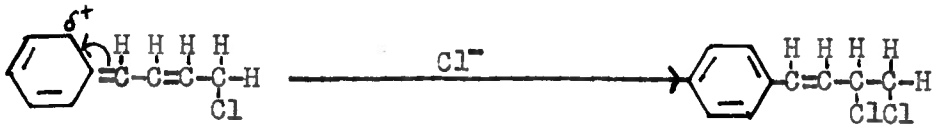
[5]Jones and Williams, J. Chem. Soc., 829 (1934).

[6]Kondakow, J. Prackt. Chem., 62, 166 (1900).

[7]Farmer, Lawrence, and Scott, J. Chem. Soc., 510 (1930).

[8]Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

[9]Straus, Ber., 42, 2866 (1909).



This behavior is understandable due to the fact that the entire unsaturation of the system is utilized in supplying electrons to carbon atom 4 which is under attack by the electrophilic reagent. The negative chlorine then attacks carbon atom 3 by virtue of its partial positivity. Only 3,4 addition permits (1) utilization of the entire conjugation system in supplying electrons, (2) retention of the resonance energy of the intact benzene ring, and (3) formation of a product in which the remaining double bond is conjugated with the benzene ring.[10]

The introduction of an electron attracting group (nitro) in the ortho or para position should decrease the stabilization due to phenyl vinyl conjugation. If this is true then we would predict that when a mole of halogen attacks 1-(p-nitrophenyl)-butadiene the amount of 3,4 addition product is decreased and the amount of 1,4 isomer increased. Hayes[11] reported that 1-(p-nitrophenyl)-2,3-dimethylbutadiene-1,3 added bromine to the 1,4 position. McCray[12] reported that the halogenation of 1-(p-nitrophenyl)-3-methyl-1,3-butadiene led to a 3,4 adduct. Hays[13] however, was unable to isolate a

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[10]Royals, op. cit., p. 403.

[11]T. Hayes, "The Bromination of 1-(P-Nitrophenyl)-2,3-Dimethylbutadiene-1,3," Unpublished Master's thesis, Atlanta University, Department of Chemistry, 1952.

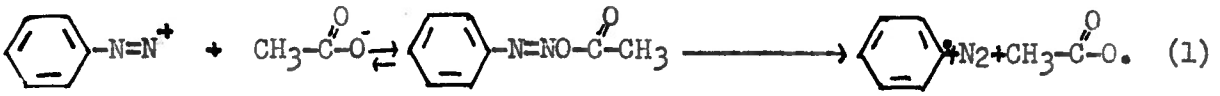
[12]William McCray, "The Bromination of 1-(P-Nitrophenyl)-3-Methylbutadiene-1,3," Unpublished Master's thesis, Atlanta University, Department of Chemistry, 1960.

[13]Matthew Hays, "The Chlorination of 1-(P-Nitrophenyl)-2,3-Dimethyl-butadiene-1,3," Unpublished Master's thesis, Atlanta University, Department of Chemistry, 1954.

dichloro compound when 1-p-nitrophenyl-2,3 dimethylbutadiene-1,3 was chlorinated in chloroform. He did obtain, instead, 1-p-nitrophenyl-2,3-dimethyl-4-chlorobutadiene-1,3.

In our study we were interested in the directive influence of the highly electronegative p-nitrophenyl group on the addition of chlorine to 3-methyl-1-p-nitrophenylbutadiene-1,3.

There are two schools of though concerning the method in which diazonium salts add to olefinic systems, which could apply equally as well to conjugated systems. Kochi[14] and Koelsh[15] believe addition proceeds by a free radical mechanism. Koelsh has postulated the following mechanism:


(1)


(2)


(3)


(4)


(5)


(6)

In view of Kochi's findings, slight modifications of the above mechanism

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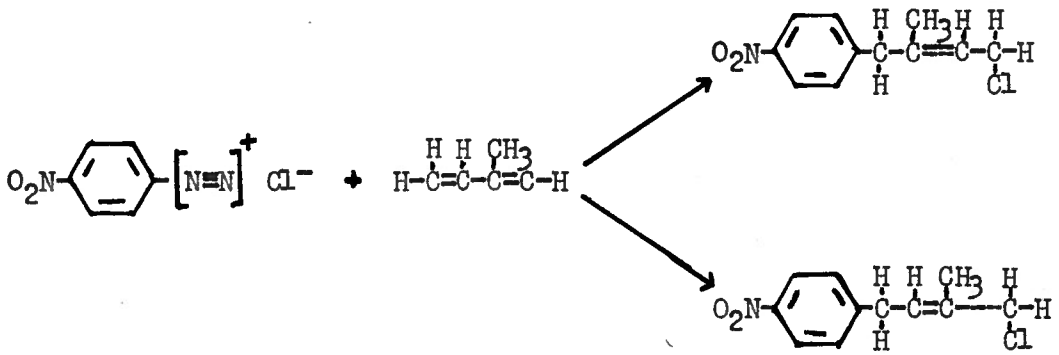
[14]Kochi, J. Am. Chem. Soc., 77, 5090, 5274 (1955).

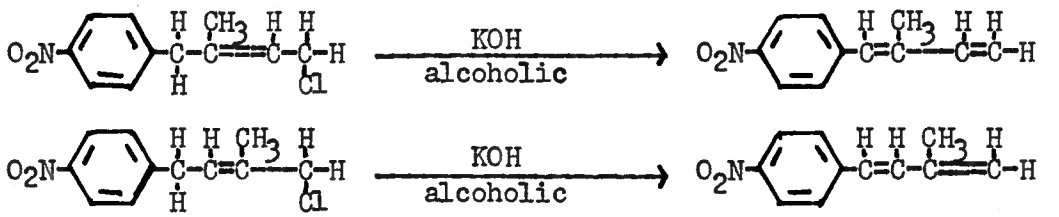
[15]Koelsh and Boekenheide, Ibid., 68, 412 (1944).

have occurred. It is now postulated that the cuprous ion, instead of the cupric ion, is the effective catalyst. Other chemists have proposed an ionic mechanism.

The diene was prepared by treating p-nitrobenzene diazonium chloride with isoprene under the conditions described by Conyer and Ropp.[16] The following equations indicate that the chlorobutenes formed resulted in the formation of 2 possible isomers:



Upon dehydrohalogenation of the chlorobutenes, the following isomers of butadiene would be obtained:



When the isomeric dienes were dehydrohalogenated yellow crystals, m.p. 79-81°, and an oil were obtained.

The Diels and Alder derivative of the diene was prepared from a small sample of the pure crystalline material and maleic anhydride. The formation

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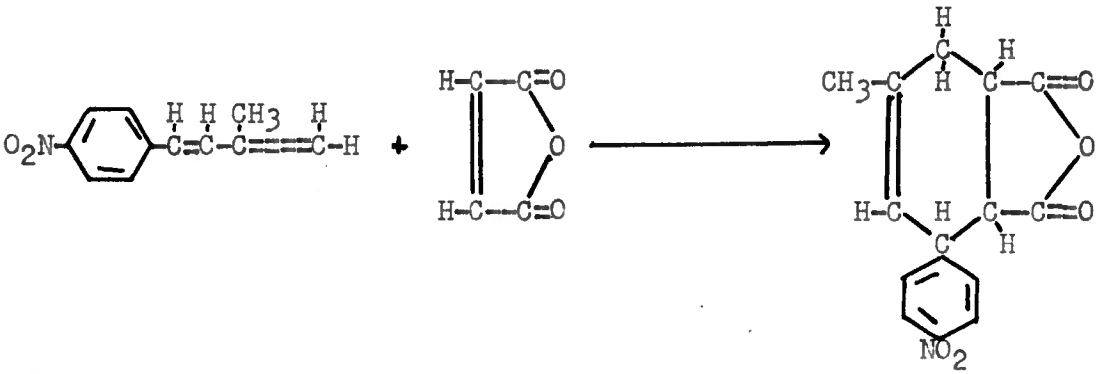
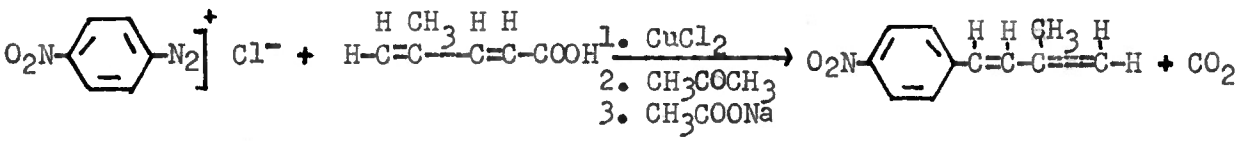
[16] Conyer and Ropp, J. Am. Chem. Soc., 70, 2283 (1948).

of this derivative may be represented by the following equation:



To determine which of the two isomers resulted from the dehydrohalogenation of the chlorobutene, we prepared the diene by the Meerwein reaction in which a diazonium salt was treated with 4-methylpentadienoic acid-1,3 using acetone as the solvent, sodium acetate as a buffer and cupric chloride as a catalyst. The following equations illustrate the preparation of 3-methyl-1-p-nitrophenylbutadiene-1,3:

4-methylpentadienoic acid-1,3



The diene prepared by this method, m.p. 79-81°, had the same melting point as the diene crystals made from the chlorobutene. This further indicates that only one chlorobutene is obtained when p-nitrobenzenediazonium chloride reacts with isoprene. The compound isolated is the one expected since Dombronskii[17] found that isoprene reacts with benzenediazonium chloride in

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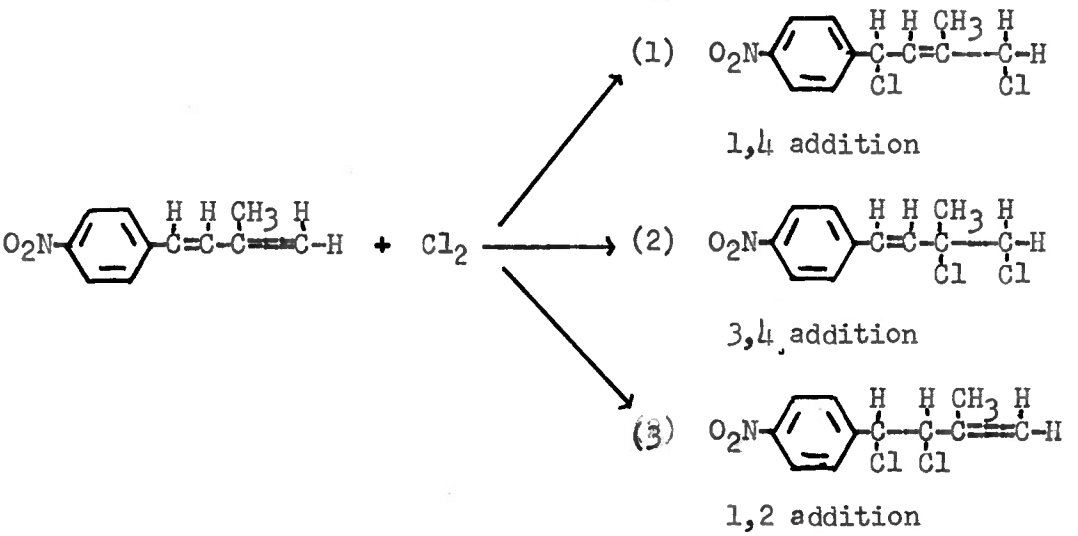
[17]Dombronskii, Chemical Abstracts, 51, 950g (1957).

the presence of acetone and cupric chloride to yield 1-phenyl-4-chloro-3-methyl-2-butene.

The diene was then chlorinated according to the method of Hellman and Hellman.[18] The following equations will illustrate the formation of the three possible dichloro compounds:



As has been previously mentioned the most stable structure would be the 3,4 adduct because it allows for p-nitrophenyl-vinyl conjugation. If the adduct had been bromine it would be expected that the halogen atom would immediately ionize and rearrange to position one. However, McCray[19] only isolated the 3,4 isomer. Chlorine forms a less mobile system[20] and it would be expected that the 3,4 isomer initially formed would rearrange less readily into the 1,4 isomeride.

The chlorination of the diene resulted in a light yellow mixture of

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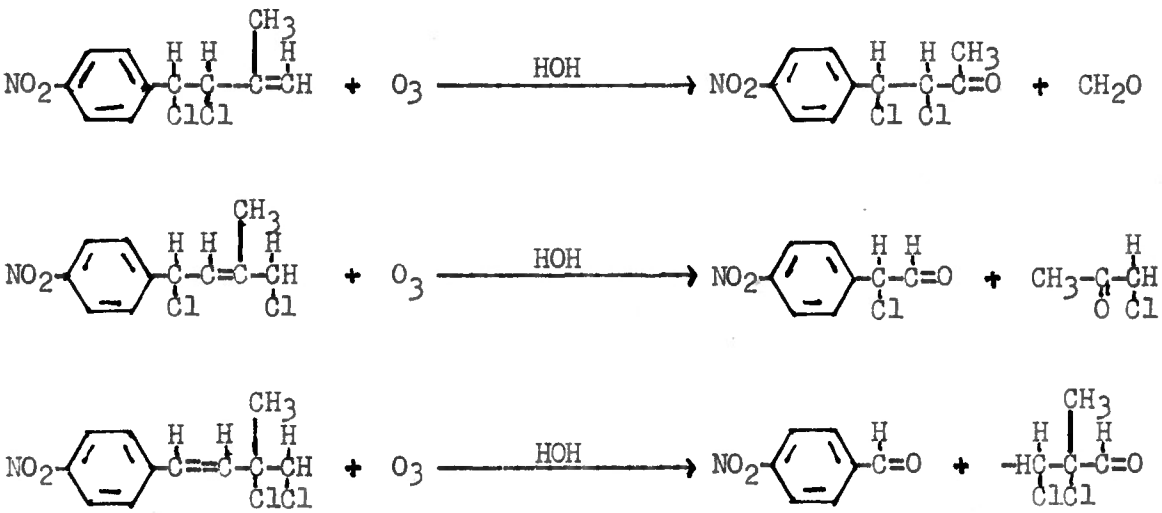
[18]Hellman, Hellman and Muslow, J. Am. Chem. Soc., 76, 1175 (1954).

[19]McCray, op. cit.

[20]De La Mare, Scott, and Robertson, J. Chem. Soc., 1168 (1947).

oil and crystals. A chlorine analysis was in accord with the theoretical for the dichlorobutene. Treatment of the dichlorobutene with sodium iodide in acetone yielded free iodine which suggests that chlorine was on adjacent carbon atoms. The dichlorobutene rapidly decolorized potassium permanganate solution and when exposed to light turned dark within 3 to 4 hours.

Ozonization of the dichlorobutene was carried out at zero degrees, using methylene chloride as the solvent, by passing ozonized oxygen through the solution. Theoretically, the following products are obtainable from the three possible dichlorobutenes:



The isolation of 1-p-nitrophenyl-1,2 dichloropropanone-2 and formaldehyde would suggest 1,2 addition; the identification of 1-p-nitrophenyl-1 chloroacetaldehyde and chloroacetone would be indicative of 1,4 addition and the identification of p-nitrobenzaldehyde and 2,3 dichloro-2 methyl-propionic aldehyde would indicate 3,4 addition.

In order to determine the nature of the ozonolysis products, the following procedure was followed: The hydrolysis mixture was extracted

with ether and the ether layer washed with a 5% solution of sodium carbonate in order to remove any acids formed in the oxidation of the dichlorobutene.

A small amount of oil and crystals (m.p. 104°-106°C) were obtained from the ether layer. The oil was separated from the crystals by decantation and filtration. The oil was purified by treating it with norit. The resulting yellow oil was found to be a lachrymator and turned dark upon standing. A few drops of the oil was treated with an acetone solution of sodium iodide. The solution yielded free iodine which indicated that chlorine was on adjacent carbon atoms. A semicarbazone derivative (m.p. 180°-182°C) and a 2,4-dinitrophenylhydrazone derivative (m.p. 108°-110°C) were obtained from the oil. Analysis of the oil for chlorine was in close agreement with those calculated for 2,3-dichloro-2-methyl propionic aldehyde.

The crystals (m.p. 104°-106°C) resulting from the original mixture gave a negative Beilstein test. A 2,4-dinitrophenylhydrazone derivative (m.p. 317°-319°C) and a semicarbazone derivative (m.p. 219°C) were obtained from the crystals. The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone derivatives were not depressed when melted with the corresponding derivatives obtained from an authentic sample of p-nitrobenzaldehyde. This evidence offered some indication that the unknown aldehyde was p-nitrobenzaldehyde.

The fact that no products or derivatives of products corresponding to formaldehyde, 1-(p-nitrophenyl)-1,2-dichloropropanone-2, 1-(p-nitrophenyl)-1-chloroacetaldehyde or chloroacetone was indicative that chlorine added predominantly to the 3 and 4 carbon positions.

EXPERIMENTAL

Reagents.--

Acetone

Chlonine

Isoprene

Ligroin

P-Nitroaniline

Cupric Chloride

Sodium Acetate

Methylene Chloride

Sodium Nitrite

Potassium Metabisulfite

Sodium Hydroxide

Ethyl Ether

Malonic Acid

Maleic Anhydride

Potassium Permanganate

Sodium Bisulfite

The Preparation of 1-(p-Nitrophenyl)-3-Methylbutadiene-1,3.--The crude 4 chloro-3 methyl 1-(p-nitrophenyl)-butene-2 was prepared according to the method of Conyer and Ropp. The diazonium salt solution resulting from diazotizing 140g (1 mole) of p-nitroaniline was treated with 140 ml of isoprene which yielded 160 grams of dark crude oil. The crude chlorobutene obtained from diazotization was dissolved in a mixture of 500 ml of ligroin (90-120°C) and 500 ml of benzene. Five grams of norit was added and the mixture was refluxed for 2 hours. After filtration, to remove norit, the solvent was removed by distillation from a steam bath. The residue was taken up in ether and filtered through a funnel filled with norit and cotton plugs. The filtrate was evaporated over a steam cone. The purified residue appeared as a dark red oil. A solution of 112 g of KOH (2 moles) in 450 ml of methanol was added from a dropping funnel during 30 minutes while the mixture was kept between the temperatures of 15°-30°C by cooling with a cold water bath. After stirring for an additional hour, the reaction mixture was then allowed to stand over night. The following morning half of the reaction mixture was transferred to a 1-liter filter flask. The filter flask was connected to a water pump and the excess methanol removed by suction. A few yellowish-brown crystals fell to the bottom of the filter flask, when the reaction mixture had been decreased to three-fourths of its original volume. The last portion of the alcoholic mixture was transferred to the filter flask and the removal of the excess solvent was continued. As crystals were formed they were continually filtered in order to decrease the probability of contamination. The Buchner funnel which contained the crude yellow crystals was transferred to another filter flask which was immediately connected to a water pump. The crystals were then dried as much as

possible in the funnel by suction for two hours. Next, the crude diene was placed in a vacuum desiccator and allowed to dry for an additional three hours.

If no crystals appeared during the suction the residue was tested for halogens. If the residual matter gave a negative test for halogen it was diluted with 400 cc of water and extracted with several small portions of ether. The ether solution was then washed with water until the aqueous layer was clear. After which the etheral layer was dried over anhydrous calcium sulfate for two hours. The ether solution was then transferred to a filter flask and the ether was removed by suction. The oily residue which remained in the flask was taken up in ligroin. The ligroin was evaporated to one-fourth of its original volume. The solution was cooled in a carbon dioxide ice-bath. After cooling for one hour, 5 grams of yellow crystals precipitated, m.p. 79-81.

The Preparation of 4-Methyl-Pentadienoic Acid-1,3[21].—To a solution of 118 g of potassium metabisulfite in about 200 cc of water, cooled in a freezing mixture, 21.7 ml of methacrolein was added, drop by drop, with continuous stirring. After all the methacrolein had been added, the stirring was continued for two hours at room temperature. Malonic acid (52 grams) was then added and the solution was refluxed for two hours. The solution was then concentrated to a thick, sirupy mass on the steam cone until the evolution of carbon dioxide had ceased. During this time the viscous mass was stirred in order to avoid excessive frothing. The residue was then dissolved in about 100 ml of water, transferred to a 1500 ml beaker. Coarsely

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[21] Muskat, Becker and Lowerstein, J. Am. Chem. Soc., 52, 329 (1930).

ground sodium hydroxide (300 grams) was gradually added with continuous stirring. It was then heated on the steam bath for 4 hours, after which it was allowed to cool. Small portions of the semi-crystallized mass were transferred to a 1-liter beaker to which was added ice. The mixture was then slowly neutralized with 25% hydrochloric acid under continuous stirring. During the neutralization ice was added to keep the temperature at about zero degrees. The acidic solution was extracted with several portions of ether and dried over sodium or calcium sulfate. The dry etheral solution was transferred to a filter flask and the ether removed by the water pump. The yellow residue (15 grams) was recrystallized from low boiling ligroin 35°-60°. The pure acid (12 grams) had a peculiar rancid odor and melted at 56-57°C. The acid was used immediately because it polymerized on standing.

The Preparation of 1-(p-Nitrophenyl)-3-Methylbutadiene-1,3[22].--p-Nitroaniline hydrochloride was prepared by heating 29 grams of p-nitroaniline, recrystallized once from ethanol, with 42.5 ml of concentrated hydrochloric acid and 124.5 ml of H_2O until the mixture became homogeneous. The mixture was cooled in an ice-salt bath and stirred rapidly in order to precipitate the hydrochloride as fine crystals. Cracked ice (100 grams) was added and a solution of 14 grams of $NaNO_2$ in 40 ml of water was added with rapid stirring during a 30 minutes period while the temperature of the mixture was held between -4° and 5° by cooling in an ice-salt bath. The mixture was stirred for an additional period of 15 minutes and then filtered through a chilled

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[22]Bergman and Weinberg, J. Org. Chem., 6, 134 (1941).

Buchner funnel into an ice cooled filter flask.

The filtrate was kept below 4°C and added dropwise during a 60 minute period to a cold, vigorously stirred mixture composed of (.2 mole) 22.4 grams of 4-methyl pentadienoic acid, 250 ml of acetone, a solution of 58 grams of sodium acetate trihydrate in 55 ml of water, and 12 grams of cupric chloride. After stirring for one hour at 0°C the reaction mixture was adjusted to a pH of 4-5.

After adjusting the pH the cooling bath was removed and the mixture was stirred for 4 additional hours. At the end of this period the reaction mixture was distilled with steam until the distillate became clear. The non-volatile residue was allowed to cool and then taken up in ether, washed with dilute sodium hydroxide, distilled water, dilute hydrochloric acid and again distilled water. The etheral solution was dried over anhydrous calcium or sodium sulfate and the ether removed by suction on the water pump. The crude crystals (7 grams) were recrystallized from petroleum ether. The pure diene 5.5 g had a melting point of 79°-81°C.

The Preparation of the Maleic Anhydride Adduct of 1-(p-Nitrophenyl)-3-Methylbutadiene-1,3.--The diene (1 gram) and 0.9 grams of maleic anhydride were dissolved in 50 ml of dry thiophene free benzene in a 500 ml round-bottomed flask. The mixture was refluxed on a steam bath for 8-10 hours. After three-fourth of the solvent was removed tan crystals appeared. Recrystallization from ligroin gave crystals melting at 140°-142°C.

Anal. Calcd. for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.52. Found: C, 62.73; H, 4.50.

The Chlorination of 1-(p-Nitrophenyl)-3-Methylbutadiene-1,3.--A solution

of chlorine (1.5 g) dissolved in 200 ml of methylene chloride was added drop by drop to a solution of 4 grams of 1-p-nitrophenyl-3-methyl-butadiene-1,3 in 200 ml of methylene chloride. Throughout the addition, which took 2.5 hours, vigorous stirring was maintained while the temperature was kept near -10°C.

The product was washed several times with a 10% solution of sodium carbonate and then water in order to remove the excess acid. It was dried overnight over anhydrous sodium sulfate. The next morning the solvent was removed by suction at the water pump. The residue was taken up in ether and treated with decolorizing carbon. The ether was removed by suction and the dichloride appeared as a mixture of oil and crystals. The mixture was not separated. It gave a positive Beilstein test and decolorized a solution of potassium permanganate. A few drops of the material were treated with a solution of sodium iodide in acetone. Free iodine was liberated which indicated that chlorine had added to adjacent carbon atoms. Yield of pure material was 2 grams.

Anal. Calcd. for $C_{11}H_{11}Cl_2O_2N$: Cl, 28.08. Found: Cl, 28.15.

The Ozonolysis of 1-(p-Nitrophenyl)-3-Methyl-3,4-Dichlorobutene-1.— A current of ozonized oxygen was passed through a solution of the dichloride (2 grams) in methylene chloride (100 ml) while the temperature was maintained at 0°C for a period of five hours. After the completion of the ozonolysis the solution remained standing for 1 hour. After this period the solution was transferred to a suction flask and the solvent removed by means of a water pump. The ozonide was decomposed by refluxing for 15 minutes. The hydrolysis mixture was extracted with ether. The etheral

solution was washed with 100 ml of a 5% solution of sodium hydroxide and dried over anhydrous sodium sulfate. The dried ether layer was filtered and the ether removed by suction. Remaining in the container after the removal of the ether was an oil and a white solid. The liquid and solid mixture was separated by filtration. White crystals (m.p. 104°-106°C), 0.5 grams, were obtained from the mixture by filtration. A small amount of oil was also obtained.

The oil was purified by dissolving it in ether and the etheral solution filtered through a funnel fitted with cotton plugs and norit. The ether was removed in a vacuum by the water pump. A yellow oil remained in the flask. The oil gave a positive Beilstein test. The oil was also found to be a lachrymator and turned dark upon standing. A few drops of the oil were treated with an acetone solution of sodium iodide. The solution yielded free iodine which indicated that chlorine was on adjacent carbon atoms. A semicarbazone derivative (m.p. 180°-182°C) and a 2,4-dinitrophenylhydrazone derivative (m.p. 108°-110°C) were obtained from the oil. The 2,4 dinitrophenylhydrazone derivative of the unknown was in close agreement with the 2,4-dinitrophenylhydrazone derivative of 2,3-dichloro-2-methylpropionic aldehyde as reported in the literature. Analysis of the oil for chlorine was in close agreement with that calculated for 2,3-dichloro-2-methylpropionic aldehyde. This evidence indicated that the unknown oil was 2,3-dichloro-2-methylpropionic aldehyde.

The crystals (m.p. 104°-106°C) resulting from the original mixture gave a negative Beilstein test. A 2,4-dinitrophenylhydrazone (m.p. 317°-319°C) and a semicarbazone derivative (m.p. 219°C) were obtained from the crystals.

The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone derivatives were not depressed when melted with the corresponding derivatives obtained from an authentic sample of p-nitrobenzaldehyde.

Anal. Calcd. for $C_7H_5NO_3$: C, 55.62; H, 3.31. Found: C, 55.68; H, 3.33.

This evidence indicated that the unknown solid aldehyde was p-nitrobenzaldehyde.

Oxidation of 2,3-Dichloro-2-Methylpropionic Aldehyde.—A saturated solution of potassium permanganate in water was added to a few drops of the aldehyde in 10 ml of water to which a few drops of 10% sodium hydroxide solution was added. The mixture was shaken vigorously and sufficient permanganate was added to impart a definite purple color. The mixture was acidified with dilute sulfuric acid and sodium bisulfite solution was added until the permanganate and manganese dioxide were converted to manganese sulfate. The acidic mixture was extracted with ether and dried over sodium sulfate. An oil was obtained after the ether was removed. This oil crystallized in an ice bath, but again turned to an oil when room temperature was reached. An S-benzylthiourium derivative was prepared and found to melt at 140°C, which was in close agreement with the derivative of 2,3-dichloro-2-methylpropionic acid as reported in the literature.[23]

The fact that when the dichloride, obtained from the chlorination of 1-p-nitrophenyl-3-methylbutadiene-1,3, was subjected to ozonolysis and hydrolysis, p-nitrobenzaldehyde and a carbonyl oil with chlorine on adjacent carbon atoms were obtained, is supporting evidence that 1-p-nitrophenyl-3-methylbutadiene-1,3 added chlorine in the 3 and 4 positions.

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[23] Ballinger and De La Mare, J. Chem. Soc., 1481-8 (1957).

SUMMARY

1-p-nitrophenyl-3-methylbutadiene-1,3 was prepared by dehydrohalogenating the chlorobutene obtained when treating p-nitro-benzenediazonium chloride with isoprene. The diene was also prepared by treating p-nitrobenzenediazonium chloride with 4-methyl pentadienoic acid-1,3.

The Diels and Alder derivative of 1-p-nitrophenyl-3-methylbutadiene-1,3 was prepared by condensing it with maleic anhydride.

The diene, 1-p-nitrophenyl-3-methylbutadiene-1,3, was treated with chlorine and the structure of the resulting dichlorobutene determined by ozonolysis. It was experimentally determined that the diene added chlorine in the 3,4 positions.

It is recommended that the dichlorobutene of the diene be ozonided within minutes after its preparation. This should be done in order to eliminate the possibility of decomposition of the dichlorobutene due to heat and exposure to light.

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